

Interactive
Comment

Interactive comment on “Secondary organic aerosol formation from reaction of tertiary amines with nitrate radical” by M. E. Erupe et al.

Anonymous Referee #2

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This work is one in a series of papers that this group of authors has recently submitted investigating secondary organic aerosol (SOA) formation from reactions of amines. These reactions may serve as an important source of SOA during the night time according to these results. In the current paper, the authors seek to establish a comprehensive chemical mechanism for the reaction of tertiary amines with the nitrate radical through the reaction of a homologous series of compounds including trimethylamine (TMA), triethylamine (TEA), and tributylamine (TBA) with both gas- and particle-phase products monitored by a proton transfer resonance mass spectrometer (PTRMS) and a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Due to the potential for these reactions to contribute to overall secondary organic aerosol burdens, this work is important and certainly within the scope of Atmospheric Chemistry and

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Physics.

The experiments seem to have been very carefully conducted and the overall quality of the data is good. However, I find myself in agreement with the previous reviewer that the bulk of the paper focuses on experimental techniques with the discussion of results comprising a minority of the paper content. As a result, the paper does not provide enough detail in regards to some key issues.

Central among these are the following:

(1) The subject of the paper is SOA formation from the reaction of tertiary amines with the nitrate radical. The experimental procedure relies on the reaction of ozone with NO₂ (reaction R2) in order to generate the nitrate radical. However, this chemistry appears to be problematic in that each of the amines investigated are reactive with ozone as evidenced by increasing particle volume concentrations following its introduction. The authors have tried to account for this by allowing the volume concentration to stabilize prior to the addition of NO. However, it appears that the presence of ozone and/or the products of its reaction with the parent amines continued to influence the SOA formation.

a) In the TMA reaction, the aerosol volume increases by $\sim 70 \text{ ug}^3/\text{cm}^3$ following the addition of NO while the m/z 60 signal changes little over the same time period. This could be due to a reaction product contributing to the signal at m/z 60. However, if we assume that 20% of the TMA remained upon addition of NO and that it reacted completely, I believe that the fractional aerosol yield would be $> 100\%$, which implies that the ozone products are contributing a significant amount to the SOA formed. The proposed mechanism does not account for this and this possibility was not discussed adequately in the paper.

b) This situation is even more pronounced in the TEA reaction system where the signal intensity for TEA almost completely disappears when ozone is added to the system. It's rebound is likely to be due to a product of the TEA-ozone reaction.

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As a result, more detailed discussion is required regarding the apparent role of ozone reaction system in the generation of SOA measured in these reactions.

(2) It seems like much cleaner results would be possible by generating nitrate radicals by photolysis of methyl nitrite, which would avoid requiring the presence of ozone. Was this considered and if so why was it not used?

a) If the current nitrate radical generating system is maintained, adding time traces of ozone, NO, and NO₂ to each of the time traces provided in Figures 1a, 2a, and 3a would be useful.

3) There was no discussion of subtracting the NO₃ reaction product spectra from the ozone reaction product spectra (e.g. are the spectra presented a combination of products from the ozone reaction and NO₃ reaction?). Again, because the focus of this paper is on the nitrate radical reaction, such subtraction is warranted in order to isolate only that spectra that is due to the nitrate reaction.

Suggested minor changes:

p. 16589, line 14: Change "After the particles exit the lens, the enter in to the particle ToF..." to "Upon exiting the lens, particles are accelerated in to the particle time-of-flight region and eventually impact on a heated oven located in the analysis chamber."

16589, line 16: Change "...then subjected to a beam of electrons..." to "...resulting vapors are then ionized with 70eV electrons before entering a time-of-flight mass analyzer..."

p. 16592, line 3: Change sentence beginning "Trimethylamine-N-oxide..." to "The triethylamine-N-oxide (TMAO, C₃H₉NO⁺) parent ion is located at nominal m/z 75."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16585, 2008.

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